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Low Band Gap Polymers Based on Benzo[1,2-*b*:4,5-*b*′]dithiophene: Rational Design of Polymers Leads to High Photovoltaic Performance

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ABSTRACT: This study centers upon the summarized four design criteria for conjugated polymer photovoltaic materials: high oxidation potential, low band gap, a planar symmetrical structure, and high molecular weight. Two polymer materials were synthesized to fulfill these design criteria, both based upon copolymers of benzo[1,2-*b*:4,5-*b*′]dithiophene (**BnDT**) and 4,7-di(2-thienyl)-2,1,3-benzothiadiazole (**DTBT**). Additional hexyl chains were added to one polymer on the 4 position of the **DTBT** unit, which increased the molecular weight of the polymer without detracting from its electrochemical or optical properties. Both polymers perform exceptionally well in preliminary bulk heterojunction solar cells, reaching power conversion efficiencies greater than 4%.

Introduction

Conjugated polymer-based solar cells have made several recent advances toward commercialization,[1] with a few polymers reaching power conversion efficiencies higher than 6% in the typical bulk heterojunction (BHJ) devices.[2−5] As impressive and important as these polymers are, they still do not meet the targeted 10% efficiency that is required for broad commercialization.[6] While improvements in device fabrication,[7] film morphology control,[8−10] and alternative acceptors to $PC_{61}BM$[11,12] will increase device efficiency, new polymer materials are still essential to bringing conjugated polymer solar cells to the mainstream commercial market.

After intensive investigation of numerous materials in the past decade, four design criteria[6,13] have emerged for the ideal candidate donor polymers to be used in BHJ devices with fullerene as the acceptor: (a) a low HOMO energy level in order to achieve a high open circuit voltage (V_{oc}); (b) a low band gap to maximize light absorption; (c) a high hole mobility, which requires a planar structure to encourage the crystallinity of the polymer;[14] (d) a high molecular weight and good solubility, to achieve the optimal morphology, in order to maximize the short circuit current (J_{sc}), and a high fill factor (*FF*). Unfortunately, though numerous low band gap materials have been synthesized, only few polymers have closely met all these criteria and demonstrated impressive efficiencies.[2,15,16] In this study, a new intramolecular charge transfer (ICT) copolymer,[17,18] poly[4,8-dialkylbenzo[1,2-*b*:4,5-*b*′]dithiophene-*alt*-4,7-di(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole] (**PBnDT-4DTBT**) was developed to fulfill these design criteria. BHJ solar cells based on the blend of this polymer and $PC_{61}BM$ demonstrated a V_{oc} of 0.81 V, a J_{sc} of 9.70 mA cm^{-2}, and a *FF* of 0.55, yielding an overall efficiency of 4.3% under 1 Sun condition (AM1.5, 100 mW cm^{-2}). To the best of our knowledge, **PBnDT-4DTBT**:$PC_{61}BM$ demonstrates one of the highest efficiencies achieved so far, under 1 sun conditions, by BHJ solar cells comprised of any single low band gap polymer blended with $PC_{61}BM$.[3,15,19]

Results and Discussion

Monomer and Polymer Synthesis. By fusing an electron deficient benzene with two flanking thiophene units, the comonomer benzo[1,2-*b*:4,5-*b*′]dithiophene (**BnDT**) offers a high oxidation potential, thereby fulfilling criterion (a). Furthermore, **BnDT** has an entirely planar and symmetrical structure, an important prerequisite in order to achieve high mobility according to part (c). For example, **BnDT**-based copolymers have recently shown high hole mobility in organic field effect transistors.[20] Several ICT copolymers based upon **BnDT** for use in photovoltaic cells have been thoroughly investigated, but power conversion efficiencies of the resulting devices remained below 1.75%.[21,22] **BnDT** has also been copolymerized with thieno[3,4-*b*]thiophene by Liang et al., and device efficiencies over 7% were obtained.[3,19] Unfortunately, the low oxidation potential of the comonomer, thieno[3,4-*b*]thiophene, established a low V_{oc}, thereby limiting the potential of this polymer to attain 10% efficiency.[6]

The remaining two design criteria, (b) a low band gap and (d) a high molecular weight and good solubility, were satisfied by the selection of the other comonomer, 4,7-di(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (**4DTBT**)[23] (Figure 1). The **DTBT**[24,25] unit is a common electron deficient comonomer, which lowers the band gap through ICT. The two additional alkyl chains in the case of **4DTBT** allow for more soluble polymers that do not precipitate during polymerization. Preventing this precipitation is critical to ensuring high molecular weight material, and the importance of molecular weight in photovoltaic materials is well documented.[26−28] Monomers similar to **4DTBT** and their utility in obtaining high molecular weight polymers have been previously studied, resulting in power conversion efficiencies below 3%.[23,29−32] However, **BnDT** is a more suitable monomer than those studied previously (e.g., fluorene) to polymerize with **4DTBT**, due to the flanking thiophenes. These thiophenes eliminate steric hindrance from the alkyl chain at the 4 position of the adjacent thiophene (Figure 1b) which is normally exhibited in the case of benzene-based monomers such as fluorenes or carbazoles that do not contain a heteroatom. This minimized steric hindrance also results in a planar conjugated backbone, leading to a small band gap and high mobility.[32]

Thus, **PBnDT-4DTBT** was synthesized using standard Stille coupling polymerization conditions, yielding a green-black solid. For comparison, **BnDT** was also polymerized

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with nonalkylated **DTBT**. Though longer branched alkyl chains were anchored on the **BnDT** of **PBnDT-DTBT**, this polymer still exhibits low molecular weight with a number-average molecular weight (M_n) of 5.6 kg/mol, likely due to precipitation of the polymer during the polymerization. Accordingly, we observed that a large quantity of solid **PBnDT-DTBT** remained in the Soxhlet thimble after extraction with chloroform. With additional solubilizing chains on the **4DTBT** unit, **PBnDT-4DTBT** displayed a higher molecular weight (M_n = 21.9 kg/mol, PDI = 4.14), ascribable to the increased solubility of this polymer.

Optical and Electrochemical Properties. Optical and electrochemical characterization of the two polymers reveals that these polymers are almost identical. The optical band gap of both polymers is 1.7 eV. **PBnDT-DTBT** demonstrates a more pronounced shoulder at approximately 650 nm (Figure 2a), which can be attributed to slightly increased π stacking and extension of the conjugation over two dimensions in the solid state.[33] CV measurements demonstrate a HOMO and LUMO energy level of −5.33 eV and −3.17 eV respectively for **PBnDT-DTBT**. In the case of **PBnDT-4DTBT**, these energy levels increase to a HOMO of −5.26 eV, and a LUMO of −2.96 eV, due to the electron releasing hexyl groups on the thiophenes of the **4DTBT** unit. The observed similarities in the optical and electrochemical properties of both polymers indicate the addition of hexyl chains to the **DTBT** unit could have an impact on the photovoltaic characteristics of the device (due to the noticeably increased molecular weight) without affecting the intrinsic semiconducting properties of the polymer.

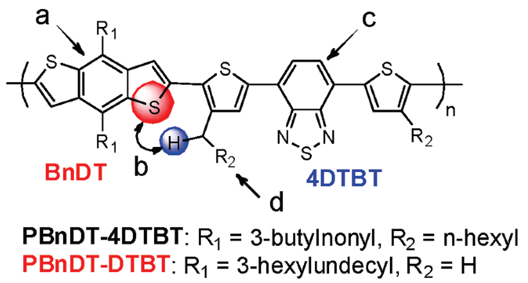


Figure 1. Structure of polymers. (a) Benzene center ring raises the oxidation potential, and planarity of **BnDT** unit encourages crystallinity. (b) Flanking thiophenes promote planarity of the polymer backbone via reduction of steric hindrance between adjacent monomer units. (c) 2,1,3-benzothiadiazole unit lowers band gap through ICT. (d) Additional alkylated positions provide high molecular weight and soluble polymer.

Photovoltaic Properties. Preliminary photovoltaic results are exceptionally promising for each of these two materials, especially for **PBnDT-4DTBT**. BHJ devices of the two polymers blended with $PC_{61}BM$ yield power conversion efficiencies breaching 3.8% (Figure 3a). Despite exhibiting a slightly higher HOMO energy level, **PBnDT-4DTBT** displays a V_{oc} of 0.81 V, only 20 mV lower than that of **PBnDT-DTBT** (0.83 V). However, the J_{sc} increases from 7.79 mA cm^{-2} of **PBnDT-DTBT** to 9.70 mA cm^{-2} in the 4-hexyl version of the polymer (**PBnDT-4DTBT**), thus re-emphasizing the importance of a high molecular weight and solubility in BHJ polymer solar cells.[26−28] Furthermore, the good solubility of **PBnDT-4DTBT** leads to a more homogeneous mixture with PCBM, while some fibrous textures were observed in the case of **PBnDT-DTBT**, possibly due to the aggregation of these low molecular weight polymers (Figure S3 in Supporting Information).

Figure 3b shows the incident photon to current efficiency (IPCE) of two BHJ thin films, together with their individual

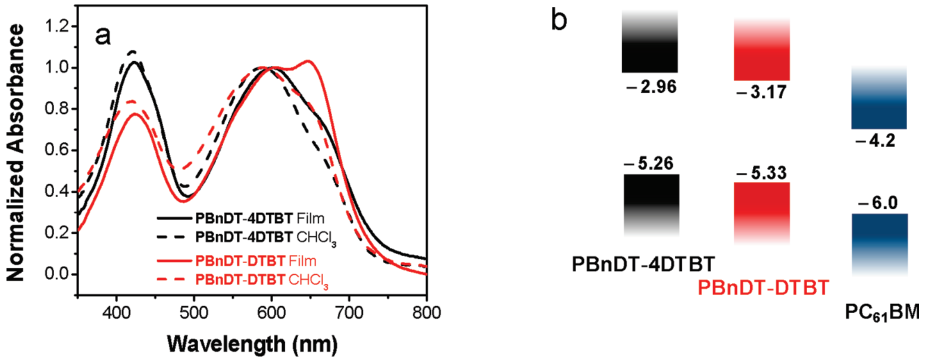


Figure 2. (a) UV−vis absorption of both polymers in chloroform solutions at room temperature and as thin films. (b) Energy band diagram (eV).

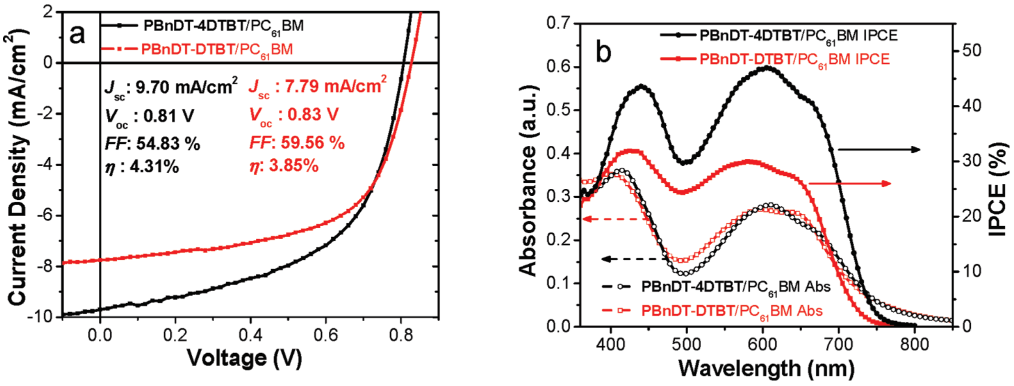


Figure 3. (a) Characteristic J-V curves of the devices of polymer-based BHJ solar cells under 1 Sun condition (100 mW/cm^2). 4.3% is one of the highest observed efficiency numbers for **PBnDT-4DTBT**-based BHJ PV devices; the average efficiency of 8 devices was over 4%. (b) IPCE and absorption of semioptimized devices.

film absorption spectra. Not surprisingly, these two thin films (~100 nm) have almost identical absorption spectra, since the two polymers have the same conjugated backbone and same blending ratio in regard to $PC_{61}BM$ (1:1). However, **the PBnDT-4DTBT**:$PC_{61}BM$ film shows a much higher IPCE of 47% than that of **PBnDT-DTBT**-based devices (30%), likely due to a high hole mobility in **PBnDT-4DTBT**:$PC_{61}BM$ devices. Mobility measurements via space charge limited current (SCLC) disclose a hole mobility of 3.8×10^{-5} cm^2 V^{-1} s^{-1} for the **PBnDT-4DTBT**:$PC_{61}BM$ device, more than double that of the **PBnDT-DTBT**:$PC_{61}BM$ device (1.6×10^{-5} cm^2 V^{-1} s^{-1}). Since these two polymers have an identical conjugated backbone (**BnDT-DTBT**), the much higher hole mobility is ascribed to the high molecular weight of **PBnDT-4DTBT**.

Conclusions

We have summarized four criteria developed from the culmination of other work[6,13] for the design of ideal polymers in order to achieve high efficiency BHJ solar cells. As a close-to-ideal polymer, **PBnDT-4DTBT** exhibits a moderate oxidation potential, possesses an entirely planar sp^2 hybridized backbone, absorbs light as low in energy as 1.7 eV, and displays moderately high molecular weight, thus satisfying the four design criteria set forth. The additional hexyl chains at the 4 positions of **DTBT** do not significantly alter the optical or electrochemical properties of the resulting polymer. Furthermore, these hexyl chains increase the molecular weight and solubility of the polymer, leading to the increased power conversion efficiency of **PBnDT-4DTBT** over that of **PBnDT-DTBT**. Both of these materials exhibit exceptionally high preliminary power conversion efficiencies with $PC_{61}BM$. Finally, only optimizations to the device thickness and polymer:$PC_{61}BM$ ratio have been attempted. Switching to $PC_{71}BM$, optimizations to the spin-casting and annealing conditions, and device fabrication improvements are all options to be explored. With further structural and device optimizations, increased power conversion efficiencies are possible in the near future.

Experimental Section

General Methods. ^1H nuclear magnetic resonance (NMR) spectra were obtained at 400 or 300 MHz as solutions in $CDCl_3$ or in $C_2D_2Cl_4$ at 100 °C. ^{13}C NMR spectra were obtained at 100 MHz as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ), and referenced from tetramethylsilane. Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet; and br, broad.

UV−visible absorption spectra were obtained by a Shimadzu UV-2401PC spectrophotometer. For the measurements of thin films, the polymer was spin-coated at 600 rpm onto precleaned glass slides from 10 mg/mL polymer solution in *o*-dichlorobenzene, and dried slowly in a Petri dish for 3 h.

Gel permeation chromatography (GPC) measurements were performed on two different machines, depending upon the solubility of the polymers in THF. For the THF soluble polymer **PBnDT-4DTBT**, a Waters 2695 Separations Module apparatus with a differential refractive index detector (at UNC Chapel Hill) was used, employing tetrahydrofuran (THF) as the eluent. For the THF insoluble polymer **PBnDT-DTBT**, a Polymer Laboratories PL-GPC 220 instrument (at University of Chicago) was used, using 1,2,4-trichlorobenzene as the eluent (stabilized with 125 ppm BHT) at 150 °C. The obtained molecular weight is relative to polystyrene standards.

Cyclic voltammetry measurements were carried out using a Bioanalytical Systems (BAS) Epsilon potentiostat equipped with a standard three-electrode configuration. Typically, a three-electrode cell equipped with a glassy carbon working electrode, a $Ag/AgNO_3$ (0.01 M in anhydrous acetonitrile) reference electrode, and a Pt wire counter electrode was employed. The measurements were done in anhydrous acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. Polymer films were drop-cast onto the glassy carbon working electrode from a 2.5 mg/mL chloroform solution and dried under house nitrogen stream prior to measurements. The potential of $Ag/AgNO_3$ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The electrochemical onsets were determined at the position where the current starts to differ from the baseline. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of polymers were calculated from the onset oxidation potential (E_{ox}) and onset reductive potential (E_{red}), respectively, according to eqs 1 and 2.

$$\mathrm{HOMO} = -(E^{ox} + 4.8\ \mathrm{eV}) \qquad (1)$$

$$\mathrm{LUMO} = -(E^{red} + 4.8\ \mathrm{eV}) \qquad (2)$$

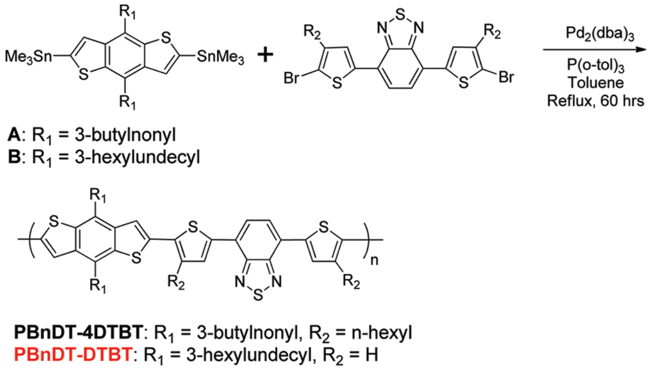
Polymer Solar Cell Fabrication and Testing. Glass substrates coated with patterned indium-doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. The 150 nm sputtered ITO pattern had a sheet resistance of 15 Ω/□. Prior to use, the substrates were ultrasonicated for 10 min in acetone followed by deionized water and then 2-propanol. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV-Ozone over 20 min. A filtered dispersion of PEDOT:PSS in water (Baytron PH500) was then spun cast onto clean ITO substrates at 4000 rpm for 60 s and then baked at 140 °C for 10 min to give a thin film with a thickness of 40 nm. A 1:1 w/w blend of polymer and PCBM at 10 mg/mL was dissolved in trichlorobenzene with heating at 140 °C overnight, filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter, and spun cast between 500−1200 rpm for 60 s onto a PEDOT:PSS layer. The substrates were then dried at room temperature under N_2 for 12 h. The devices were finished for measurement after thermal deposition of a 30 nm film of calcium and a 100 nm aluminum film as the cathode at a pressure of $\sim 1 \times 10^{-6}$ mbar. There are eight devices per substrate, with an active area of 12 mm^2 per device. The thicknesses of films were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW/cm^2 (Oriel 91160, 300 W) calibrated by a NREL certified standard silicon cell. Current versus potential ($I-V$) curves were recorded with a Keithley 2400 digital source meter. EQE were detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp) and the calibration of the incident light was performed with a monocrystalline silicon diode. All fabrication steps after adding the PEDOT:PSS layer onto ITO substrate, and characterizations were performed in gloveboxes under nitrogen atmosphere. For mobility measurements, the hole-only devices in a configuration of ITO/PEDOT:PSS (45 nm)/polymer−PCBM/Pd (40 nm) were fabricated. The experimental dark current densities J of polymer: PCBM blends were measured when applied with voltage from 0 to 6 V. The applied voltage V was corrected from the built-in voltage V_{bi} which was taken as a compensation voltage $V_{bi} = V_{oc} + 0.05$ V and the voltage drop V_{rs} across the indium tin oxide/poly(3,4-ethylene-dioxythiophene): poly(styrenesulfonic acid) (ITO/PEDOT:PSS) series resistance and contact resistance, which is found to be around 35 Ω from a reference device without the polymer layer. From the plots of $J^{0.5}$ vs V (Supporting Information), hole mobilities of copolymers can be deduced from

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer which is assumed to be around 3 for the conjugated polymers, μ_h is the hole mobility, V is the voltage drop across the device, and L is the film thickness of active layer.

AFM Images were taken using an Asylum Research MFP3D Atomic Force Microscope.

Reagents. Anhydrous toluene was purchased from EMD Chemical and used as received. Trimethyltin monomers **A** and **B** were synthesized using modified literature procedures and proton NMR spectra are provided below.[20,34] 4,7-Dithien-2-yl-2,1,3-benzothiadiazole (**DTBT**) and 4,7-di(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (**4DTBT**) were synthesized according to established literature procedures.[35,36] All other chemicals were purchased from commercial sources (Acros, Alfa Aesar, Aldrich, Fisher Scientific) and used without further purification.



Polymerization of PBnDT-4DTBT. 4DTBT (212 mg, 0.338 mmol), 2,6-bis(trimethyltin)-4,8-di(3-butylnonyl)[1,2-b:4,5-b′]-dithiophene (304 mg, 0.345 mmol), tri-*o*-tolylphosphine (13 mg, 0.406 mmol), and toluene (14 mL) were combined in a dry flask, and purged with argon for 20 min. $Pd_2(dba)_3$ (5 mg, 0.0051 mmol) was then added, and the toluene solution was purged for an additional 15 min. The reaction mixture was then heated to reflux, and stirred for 60 h, before being precipitated into rapidly stirring methanol. The resulting slurry was then filtered into a Soxhlet thimble, and extracted extensively with methanol, ethyl acetate, hexanes, and chloroform. The chloroform fraction was then concentrated under a stream of argon, and precipitated into methanol at −55 °C. The slurry was filtered, washed with methanol, and air-dried. The green-black solid was then collected, and dried under vacuum at 0.7 mmHg for 24 h. Yield = 276 mg (80%) of a green-black solid. ^1H NMR ($C_2D_2Cl_4$, 400 MHz, δ): 8.13 (s, 2H), 7.95 (s, 2H), 7.65 (s, 2H), 3.26 (s, 4H), 3.09 (br s, 4H), 1.92 (br s, 8H), 1.48 (m, 52H), 0.99 (m, 12H). Anal. Calcd for $C_{62}H_{86}N_2S_5$: C, 73.03; H, 8.50; N, 2.75. Found: C,72.99; H, 8.57; N, 2.71. GPC (THF at room temp.): M_n = 21.9 kg/mol, M_w = 90.7 kg/mol, PDI = 4.14. **PBnDT-DTBT** was prepared in a similar fashion, using an equimolar amount of **DTBT** instead of **4DTBT.**

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Supporting Information Available: Figures showing NMR spectra of molecules, CV curves, $J^{0.5}$ vs V plots of mobility measurement of polymers, and AFM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323.
(2) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297.
(3) Liang, Y.; Feng, D.; Wu, Y.; Tsai, S.-T.; Li, G.; Ray, C.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 7792.
(4) Hou, J.; Chen, H.-Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586.
(5) Chen, H.-Y.; Hou, J.; Zhang, S.; Liang, Y.; Yang, G.; Yang, Y.; Yu, L.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649.
(6) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.
(7) Chen, L.-M.; Hong, Z.; Li, G.; Yang, Y. *Adv. Mater.* **2009**, *21*, 1434.
(8) Yang, X.; Loos, J. *Macromolecules* **2007**, *40*, 1353.
(9) Peet, J.; Senatore, M. L.; Heeger, A. J.; Bazan, G. C. *Adv. Mater.* **2009**, *21*, 1521.
(10) Moulé, A. J.; Meerholz, K. *Adv. Funct. Mater.* **2009**, *19*, 3028.
(11) Ross, R. B.; Cardona, C. M.; Guldi, D. M.; Sankaranarayanan, S. G.; Reese, M. O.; Kopidakis, N.; Peet, J.; Walker, B.; Bazan, G. C.; Van Keuren, E.; Holloway, B. C.; Drees, M. *Nat. Mater.* **2009**, *8*, 208.
(12) Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; van Hal, P. A.; Janssen, R. A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3371.
(13) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58.
(14) Ohkita, H.; Cook, S.; Astuti, Y.; Duffy, W.; Tierney, S.; Zhang, W.; Heeney, M.; McCulloch, I.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 3030.
(15) Wang, E.; Wang, L.; Lan, L.; Luo, C.; Zhuang, W.; Peng, J.; Cao, Y. *Appl. Phys. Lett.* **2008**, *92*, 033307.
(16) Chen, C.-P.; Chan, S.-H.; Chao, T.-C.; Ting, C.; Ko, B.-T. *J. Am. Chem. Soc.* **2008**, *130*, 12828.
(17) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315.
(18) Zhu, Y.; Champion, R. D.; Jenekhe, S. A. *Macromolecules* **2006**, *39*, 8712.
(19) Liang, Y.; Wu, Y.; Feng, D.; Tsai, S.-T.; Son, H.-J.; Li, G.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 56.
(20) Pan, H.; Li, Y.; Wu, Y.; Liu, P.; Ong, B. S.; Zhu, S.; Xu, G. *J. Am. Chem. Soc.* **2007**, *129*, 4112.
(21) Hou, J.; Park, M.-H.; Zhang, S.; Yao, Y.; Chen, L.-M.; Li, J.-H.; Yang, Y. *Macromolecules* **2008**, *41*, 6012.
(22) Price, S. C.; Stuart, A. C.; You, W. *Macromolecules* **2010**, *43*, 797.
(23) Zhou, H.; Yang, L.; Xiao, S.; Liu, S.; You, W. *Macromolecules* **2010**, *43*, 811.
(24) Jayakannan, M.; Van Hal, P. A.; Janssen, R. A. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2360.
(25) Hou, Q.; Xu, Y.; Yang, W.; Yuan, M.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2002**, *12*, 2887.
(26) Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J. *Chem. Mater.* **2005**, *17*, 2175.
(27) Bijleveld, J. C.; Zoombelt, A. P.; Mathijssen, S. G. J.; Wienk, M. M.; Turbiez, M.; de Leeuw, D. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16616.
(28) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. *Nat. Chem.* **2009**, *1*, 657.
(29) Wang, E.; Wang, M.; Wang, L.; Duan, C.; Zhang, J.; Cai, W.; He, C.; Wu, H.; Cao, Y. *Macromolecules* **2009**, *42*, 4410.
(30) Shi, C. J.; Yao, Y.; Yang, Y.; Pei, Q. B. *J. Am. Chem. Soc.* **2006**, *128*, 8980.
(31) Song, S.; Jin, Y.; Kim, S. H.; Moon, J.; Kim, K.; Kim, J. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2008**, *41*, 7296.
(32) Qin, R.; Li, W.; Li, C.; Du, C.; Veit, C.; Schleiermacher, H.-F.; Andersson, M.; Bo, Z.; Liu, Z.; Inganäs, O.; Wuerfel, U.; Zhang, F. *J. Am. Chem. Soc.* **2009**, *131*, 14612.
(33) Brown, P. J.; Thomas, D. S.; Köhler, A.; Wilson, J. S.; Kim, J.-S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 064203.
(34) Pan, H.; Li, Y.; Wu, Y.; Liu, P.; Ong, B. S.; Zhu, S.; Xu, G. *Chem. Mater.* **2006**, *18*, 3237.
(35) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.
(36) Hou, Q.; Zhou, Q.; Zhang, Y.; Yang, W.; Yang, R.; Cao, Y. *Macromolecules* **2004**, *37*, 6299.